

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY IN SUPPORT OF UPPER ATMOSPHERIC RESEARCH

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Abstract This paper describes the laboratory program in millimeter and submillimeter spectroscopy at the Jet Propulsion Laboratory (JPL). The program directly supports ongoing and developing field measurement programs; in particular, the Microwave Limb Sounder (MLS) now in orbit aboard the Upper Atmospheric Research Satellite (UARS), the balloon borne Submillimeter Limb Sounder (SLS), the Far Infrared Limb Observing Spectrometer (FILOS), the 2.5 THz balloon OH spectrometer (BOH), and the MLS to be flown in 2002 on the Earth Observing System (EOS) AQUA platform. This program provides frequencies, linewidths and transition moments for species sought by the observing program, which have promise of being observed by instrumentation being developed by NASA, and which improved atmospheric models indicate are important. These data along with pertinent data available from other sources are analyzed and the results made available to the user community via the JPL "Microwave, Millimeter, and Submillimeter Spectral Line Catalog." From these data, accurate brightness temperatures and line profiles can be obtained. In addition, this program supplies necessary microwave through far infrared data that aid in the interpretation and assignment of infrared and optical spectra of importance to stratospheric research. Particular attention is paid to molecules whose high resolution infrared spectra are contained in the JPL and HITRAN infrared databases and to transient species relevant to research being done by the JPL kinetics group. This program has also been concerned with the determination of molecular structures and other molecular properties of halogen oxides and oxo-acids which affect chemical reactivity.

Introduction

NASA has a large ongoing stratospheric research program. In this program JPL has a leading role in the observation of millimeter wave thermal emis-

sion of stratospheric species and the development of instrumentation to perform those measurements at increasing sensitivity and at higher frequencies. Millimeter wave radiometers have been successfully flown by JPL on aircraft, balloons, and UARS. A submillimeter radiometer has made a number of successful balloon flights and submillimeter channels will be used on the MLS to be flown on the 2002 AQUA platform of EOS. The FILOS far infrared radiometer has measured OH and other species near 3.1 THz and a heterodyne channel near 2.5 THz will be part of the EOS MLS. JPL was responsible for the high resolution infrared Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) experiments and is now responsible for the planned Tropospheric Emission Spectrometer (TES) to be flown on the AQUA platform in 2002. The JPL infrared spectroscopists who provide the supporting spectroscopic studies and analyses are highly regarded by the international community. The JPL Kinetics Group has played a prominent role in characterizing many of the major stratospheric chemical processes. We have worked closely with the investigators responsible for both field measurements and other laboratory programs on a wide variety of problems in upper atmospheric research.

The millimeter spectroscopy laboratory benefits from having a strong technology development program at JPL, and from regular interaction with the MLS team, the infrared spectroscopists, and the chemical kinetics group. Throughout the course of this program we have collaborated with a number of workers on a variety of problems requiring the application of spectroscopic techniques and analysis to upper atmospheric research. Under other tasks the millimeter spectroscopy laboratory has supported observational programs in interstellar and planetary radio astronomy. In this way a rather modestly funded task has been able to provide essential and efficient support to the NASA Upper Atmospheric Research Program.

In this paper some of the past accomplishments of the laboratory program will be described in terms of its contributions to MLS support, infrared analysis, and spectroscopy of reactive species. Some of the projects currently underway will be itemized. It is hoped that the information will suggest productive areas of research for those interested in carrying out laboratory studies.

MLS Support

The JPL Submillimeter–Microwave Spectroscopy Laboratory has supported the field measurements program closely in supplying the basic spectroscopic parameters necessary for the interpretation of Earth's atmospheric spectra since 1976. The interpretation of MLS data has relied heavily on measurements and calculations of molecular spectra carried out under this program. The MLS web page (<http://mls.jpl.nasa.gov>) contains links to several documents which describe the goals of MLS program as well as some of the requirements for

laboratory data. Among the most important contributions have been a number of studies of ClO,¹⁻⁴ and O₃⁵⁻¹⁰. The ClO work has provided both the positions and air broadened linewidths that have been used for observations at both 204 and 649 GHz. The ozone data in particular have been essential to the observing community as ozone is the principal source of interfering features throughout the millimeter region. This body of data has continued to be a principal driver in the selection of observing objectives and design parameters for the field measurement program.

This program has made significant contributions to the JPL "Microwave, Millimeter and Submillimeter Spectral Line Catalog"^{11,12} which is a principal source of line position and strength information for the millimeter and far infrared field measurement community. This involves not only original measurements in our laboratory, but critical evaluation of literature data. Air broadened linewidths, although very important for analyses of atmospheric data, are not included. There are relatively few reliable linewidth measurements in the literature in the microwave and infrared regions. Significant developments in linewidth measurement technique are described by Belov and Tretyakov elsewhere in this volume. The importance of the catalog is so well recognized that our colleagues have frequently made their measurements available to us prior to publication. Waters has utilized the catalog extensively in his chapter on microwave limb sounding¹³ and has described in some detail the importance of a program in molecular spectroscopy to the field.

The catalog was initiated more than twenty five years ago as an astrophysics supported line list by R. L. Poynter. During the definition phases of the UARS Microwave Limb Sounder experiment, R. K. Kakar was supported to develop line lists for molecules of atmospheric importance. This work was continued by H. M. Pickett. Since there was some overlap of the two line lists, Poynter and Pickett merged the lists into a single catalog that was made available to other groups. The catalog has been of great use to those studying the millimeter and far infrared regions, and portions of it have been incorporated into the HITRAN compilations.¹⁴ The ongoing task in support on upper atmospheric research has devoted a considerable portion of its resources to providing data and computations for the catalog although it does not directly support distribution or software development. At present, continuously updated versions as well as much of the software used for performing the spectroscopic analyses¹⁵ are available via anonymous FTP and on the internet directly from our laboratory (<http://spec.jpl.nasa.gov>). A paper describing the newest version of the JPL Submillimeter, Millimeter, and Microwave Spectral Line Catalog was published recently¹².

We have provided important original contributions for a number of molecules of atmospheric importance and of importance to our understanding of halogen oxide chemistry. These include O₃^{5-10,16}, ClO¹⁻⁴, ClOOCl¹⁷,

ClOClO₂¹⁸, ClClO₂^{19,20}, HOCl²¹, HOClO₃²², OClO²³, BrO^{24,25}, BrOBr^{26,27}, OBrO^{26,28}, HOBr²⁹⁻³¹, OH³², H₂O₂³³, *a*¹Δ O₂^{34,35}, O₂³⁶, CO³⁶, HNO₃³⁷, ClONO₂³⁸, HO₂NO₂³⁹, COF₂^{40,41}, SO₂⁴², IO⁴³, OIO⁴⁴, and FClO⁴⁵. Spectra of all those species that may be observed *in situ* have been placed in the JPL catalog. Others are being prepared for entry in order to generate a more comprehensive database for those engaged in laboratory studies. In addition a number of new submillimeter and far infrared transitions have been measured for a variety of molecules in order to improve the reliability of frequency predictions in the far infrared region for cataloging purposes. For many of the species, the original data files used in the generation of the catalog entries are available from our web site.

Molecules for which calculations have been recently entered or improved in the catalog include O³⁵ClO, O³⁷ClO, O⁷⁹BrO, O⁸¹BrO, CO, ¹³CO, C¹⁷O, C¹⁸O, H₂O (ground state and $\nu_2=1$), ⁷⁹BrO (ground state and $\nu=1$), and ⁸¹BrO (ground state and $\nu=1$). Calculations for IO and OIO have been prepared, but are not yet available for distribution. ClClO₂ (chloral chloride) and HOClO₃ (perchloric acid) calculations have been performed, but have not been placed in the catalog. In addition, we have observed a number of previously unmeasured transitions of the rarer isotopes of water in the 550 - 700 GHz region. These include HDO (ground state and $\nu_2=1$), D₂O (ground state and $\nu_2=1$), H₂¹⁷O (ground state and $\nu_2=1$), HD¹⁸O, and H₂¹⁸O. Improved catalog entries are in preparation. In collaboration with other laboratories, a paper on the rotational spectra of SO₂, ³³SO₂ and SO¹⁷O has been published⁴¹ which extends the range of observations and improves the molecular parameters.

The spectrometer used for most of this work has been described in a number of the above referenced papers. The basic spectrometer is described in Refs. 17 and 18. THz laser sideband measurements are reported in Refs. 32 and 46. The new difference frequency spectrometer with capability from several hundred GHz to the THz region is described in Refs. 47 - 49. Recently, we have incorporated 110 - 270 GHz and 570 - 720 GHz, phase locked backward wave oscillators (BWO) for use with our submillimeter spectrometer. We have made appropriate modifications in the modulation schemes and sweeping software so that the tube can be used for precise frequency and linewidth measurements. Similar systems are described by Belov and Tretyakov in this volume. In addition, we have successfully used planar antiparallel pair Schottky diode multipliers designed and built by P. H. Siegel of the Submillimeter Wave Advanced Technology Group to observe spectra near 919.31 GHz. The multiplier generated thirteenth harmonic of ≈ 70.716 GHz using ≈ 10 mw of fundamental klystron power. These planar multipliers were also used to follow commercially available multipliers and frequency synthesizers to generate a wide range of submillimeter frequencies. Recently we have used them in an astrophysics supported program to produce 10 GHz long scans in the 525 GHz region. In

this case the synthesizer operated near 12.5 GHz and was followed by a commercial times six multiplier. The JPL multiplier was then tuned to optimize seventh harmonic. The result was forty-second harmonic of a synthesized frequency. The reproducibility of scans taken with these devices and synthesized frequencies will be particularly useful for linewidth measurements. For frequency measurements, scans of ≈ 20 GHz can be carried out unattended with subsequent automated peak measurement.

Linewidth measurements in our laboratory are usually done by using the convolution method developed by Pickett⁵⁰. Application of this method to the atmospheric molecules O_3 and ClO may be found in Refs. 4 and 9. More recently, in a collaborative effort with the De Lucia group at Ohio State University we studied the N_2 and O_2 broadening of several transitions of HNO_3 which contribute to the background emission observed by MLS³⁷. The MLS team has used these measurements interpret the background emission in terms of upper atmospheric HNO_3 distribution.^{51,52} The joint study represents one of the few examples for which different investigators using different techniques have measured identical transitions in order to validate the results⁵³. The comparison of results showed an absolute accuracy of $\approx 3\%$ can be readily obtained.

Since the strength of a rotational transition is dependent upon the individual components of the permanent molecular dipole moment, it is important to measure the dipole moment of new molecules. The techniques for doing this in the microwave region at low frequencies and for well resolved Stark effect are extensively documented in the literature. In the millimeter and submillimeter wavelength regions the measurements are complicated by the fact that the transitions are often high J transitions with unresolvable Stark effect. Moreover, the type of large diameter cells which are frequently used for observations of highly reactive species are not compatible with the application of a strong homogeneous electric field. The polarization of the high frequency radiation is not usually exactly known with respect to the applied electric field.

We have developed a technique for measuring dipole moments under weak field conditions for which the Stark effect is unresolved and with a linewidth and the microwave polarization is not well known. In one conducts an experiment using a double pass cell, the rooftop reflector used to obtain two passes through the sample also rotates the reflected radiation by 90° . Therefore, it is reasonable to assume that the the Stark shifted transition contains equal contributions from the $\Delta M = 0$ and $\Delta M = \pm 1$ components. For second order Stark shifts of the energy levels of the form

$$\Delta E/\mathcal{E}^2 = A + BM^2$$

the shift in frequency can be expressed in closed form as the intensity weighted average of all the Stark components. Here A and B are the Stark coefficients

and \mathcal{E} is the applied electric field. For the present case of equal parallel and perpendicular polarization, one obtains

$$\Delta\nu/\mathcal{E}^2 = \Delta A + \Delta B[8J(J+1) - 1]/20$$

for $\Delta J = 0$ with ΔA and ΔB referring to the differences between upper and lower states and

$$\Delta\nu/\mathcal{E}^2 = \pm[\Delta A + \Delta B J(6J+7)/20 + B_{J+1}(J+1)/2]$$

for a $J+1 \leftarrow J$ or $J \leftarrow J+1$ transition where $\Delta A = A_{J+1} - A_J$ and $\Delta B = B_{J+1} - B_J$. The upper sign is for $J+1 \leftarrow J$ and the lower for $J \leftarrow J+1$. For individual hyperfine transitions, F is to be used instead of J .

Because the distribution of microwave power in the sample cell is a function of frequency and not well controlled and because the applied field is not very homogeneous, the transitions which are used for calibration should be preferably in the same frequency region as those used for the dipole determination. While this method is not as accurate or precise as measurements of individual components, it is quite useful when more conventional techniques are unavailable. Applications of the method can be found in Refs. 20 and 28.

Infrared Analysis

In general, the contributions of rotational spectroscopy to infrared analysis are precise rotational and centrifugal distortion constants as well as very accurate rotational energies for the ground vibrational states and often excited states as well. These can be extremely useful in assigning complex infrared spectra. Merged fits of infrared and rotational data usually provide excellent molecular constants. Infrared analyses in the literature which utilize rotational data, energy levels, or molecular constants from this laboratory include works on O_3 , COF_2 ^{40,54,55}, ClO ⁵⁶, HOBr ^{29,30} and HOClO_3 ⁵⁷. The large body of HNO_3 rotational data obtained by the De Lucia group⁵⁸⁻⁶⁵ has also been used extensively. Analyses of O_3 and HNO_3 have been recently reviewed by Flaud and Bacis⁶⁶ and Perrin,⁶⁷ respectively. Currently, we are re-examining the line strengths of the ν_9 and $2\nu_5$ bands on HNO_3 using continuously flowing anhydrous samples⁶⁸.

Recently we have provided G. C. Toon with new calculations of the ν_5 band of phosgene, COCl_2 . These calculations which utilized earlier rotational data obtained from the literature have allowed the definitive identification of the COCl_2 molecular signature in high-resolution spectra taken by the MKIV balloon borne FT spectrometer⁶⁹.

Spectroscopy of Reactive Species

In addition to supporting the observing programs, we are continuing to collaborate with the kinetics group at JPL in order to unambiguously identify and characterize reactive and transient species that play important roles in upper atmospheric chemistry. Our early efforts led to the first assigned high resolution spectra and structural determination of ClOOCl ¹⁷ and ClOClO_2 ¹⁸. These remain the only high resolution studies of these compounds. Subsequently we were able to synthesize the second most stable form of a Cl_2O_2 molecule, chloral chloride and determine its structure and many of its molecular properties.^{19,20} We were also able to re-examine spectra taken in our studies of ClOOCl and ClOClO_2 and show the ClClO_2 did not form in observable quantities from the ClO self reaction or from $\text{Cl} + \text{OClO}$ under the conditions of temperature and pressure described in our earlier work^{17,18}. The determination of the ClOOCl structure was an important piece of confirming evidence that the peroxide is the primary product of the ClO self reaction and an important contributor to polar ozone depletion processes.

Most of the unstable molecules that we have studied have been referred to above. These are primarily the halogen oxides and oxoacids. The analyses of these spectra have revealed significantly more detail about the molecular structure and chemical bonding in these compounds than was previously known. In addition, spectra of the starting materials ClF_3 and FClO_2 ⁷⁰, taken during studies of FClO and ClClO_2 were analyzed in great detail by H. S. P. Müller at Universität zu Köln after he left JPL.

Recent work on unstable molecules has included the following:

1. A thorough analysis of the rotational spectra of the four main isotopic species of chloryl chloride, ClClO_2 ²⁰.
2. The analysis of the microwave spectra of the Coriolis coupled ν_4 and ν_6 states of ClClO_2 .
3. Observations of the microwave spectrum and Stark effect of FClO ⁴⁵ and determination the dipole moment.
4. Observation of the rotational spectra of the $X_1 \ ^2\Pi_{3/2}$ state of IO up to $v = 13$ and extension of the region of observations to $\approx 700 \text{ GHz}$ ⁴³.
5. The first observation of the rotational spectrum of the $X_2 \ ^2\Pi_{1/2}$ state of IO and its excited vibrational states up to $v = 9$ and the first rotational spectra of I^{18}O in both the X_1 and X_2 states⁴³.
6. Observation and analysis the first rotational spectra of OIO in the ground vibrational state and first excited bending state. This is the only high-resolution study of the molecule⁴⁴.
7. Observation of BrO rotational spectra up to $v = 8$ and $v = 7$ in the X_1 and X_2 states respectively and submitted the results for publication²⁵.

8. Observation of the rotational spectrum of ClO up to $v = 2$ as well as Cl^{18}O in natural abundance⁷¹.

The chloral chloride paper reports the synthesis, rotational spectra of the four major isotopic species, molecular structure, harmonic force field, quadrupole coupling constants, and dipole moment. A paper is in preparation in collaboration with H. S. P. Müller on rotational spectra of the Coriolis coupled ν_4 and ν_6 states. ClOClO_2 , ClClO_2 , and FCIO_2 ^{70,72,73} are all characterized by a long weak bond to the ClO_2 group. FCIO also has a weaker than normal FCl bond.

The FCIO work was done in collaboration with Müller, who has recently reported an analysis of the ν_1 and ν_2 infrared bands⁷⁴. The primary contribution of the JPL work was a determination of the molecular dipole moment. The spectra taken at JPL have been analyzed along with those taken at Köln, infrared spectra taken at Wuppertal, and molecular beam spectra taken at Zürich. Together these give a rather complete picture of the molecule. Dr. Müller has continued work on the molecule at Universität zu Köln. The primary objective of the present work is determination of molecular parameters for comparison with recent *ab initio* studies⁷⁵⁻⁷⁷.

The work on the halogen monoxides was not intended to be extensive, but we discovered during our studies of the IO rotational spectrum that very highly excited vibrational states were being formed in a chemiluminescent reaction of molecular iodine with oxygen atoms. We were initially able to follow the transitions up to $v = 12$ in the $X_1\ ^2\Pi_{3/2}$ electronic state using O atoms produced in an external microwave discharge. It is interesting the $v = 12$ state is approximately the same energy as the $a\ ^1\Delta_g$ state of O_2 and the $^2P_{1/2}$ state of atomic I. It is well known that energy exchange between $\text{O}_2\ a\ ^1\Delta_g$ and I atom is the mechanism that drives the high power chemical oxygen iodine lasers (COIL). The reaction $\text{O} + \text{I}_2 \rightarrow \text{IO} + \text{I}$ is not exothermic enough to populate states higher than $v = 10$. Earlier experiments with ClO and BrO using the products of an O_2 discharge plus the halogen molecules did not appear to give anomalous vibrational distributions. Using a dc discharge through a flowing mixture of I_2 and O_2 in the sample cell we were able to make the first observations of rotational spectra of the $X_2\ ^2\Pi_{1/2}$ electronic state. At present, we have observed vibrational levels up to $v = 13$ for $X_1\ ^2\Pi_{3/2}$ and $v = 9$ for $X_2\ ^2\Pi_{1/2}$. In addition, I^{18}O has been observed for both the X_1 and X_2 states up to $v = 5$.

Using the dc discharge cell that was so effective for vibrational excitation of IO, measurements of BrO have now been extended up to $v = 8$ and $v = 7$ for the X_1 and X_2 states, respectively. Excited vibrational levels of ClO were not obtained with these methods, however good signal to noise at thermal populations allowed measurements for the $v = 2$ levels of both the X_1 and X_2 states as well as ^{18}O in natural abundance.

The Hamiltonian of Brown, *et. al.*⁷⁸, with explicit isotope dependencies for each parameter, has provided a set of mass and nuclear moment independent parameters for each of the halogen monoxide species, IO, BrO and ClO. The electron spin-rotation constant, γ , and the centrifugal distortion of the spin-orbit splitting, A_D , which are normally correlated, have been separately determined by the isotope dependence of their contributions to the spectrum. Interatomic potentials have been derived from the mass-independent parameters that are accurate up to the observed excitation energies for each molecule. The hyperfine parameters have been compared with the literature values^{79–81} of the appropriate calculated relativistic radial integrals of the halogens.

During the IO investigation, a large number of unidentified lines appeared which we suspected might be OIO. We pursued this investigation and were successful in obtaining the first rotational and only high-resolution spectrum of OIO. OIO is an asymmetric prolate rotor ($\kappa = -0.690$) with a 2B_1 electronic ground state. It was formed initially from the products of a microwave discharge in O₂ passing over molecular iodine and later with greater yield in a DC discharge through a mixture of O₂ and I₂ vapor. Although the experiment was hampered by copious solid deposits and apparently inefficient production of OIO, the rotational spectrum was quite prominent in survey scans in the millimeter and submillimeter regions. Facilitated by predictions of fine and hyperfine patterns from ESR results⁸², it was eventually possible to identify high J , R branch transitions with $K_c \approx J$. Over 550 ground state transitions and over 160 transitions of the excited bending state have been included in the fits. The transitions cover a wide range of rotational quantum numbers and permit the accurate determination of an extensive set of molecular parameters. The parameters have been interpreted in terms of the molecular geometry, harmonic force field, and electronic structure.

Continuing Work

During the last year the MLS science team listed its highest priorities for laboratory measurements of air broadened linewidths. These are as follows:

2.5 THz lines of OH, O₂, and H₂O to improve accuracy of OH measurement (OH: 2.510 THz and 2.514 THz; O₂: 2.502 THz; H₂O: 2.532 THz).

HCl line at 625.9 GHz to improve accuracy of chlorine loading measurement.

¹⁸O¹⁶O (isotopic O₂) line at 233.9 GHz to improve accuracy of temperature measurement.

O₃ lines to improve accuracy of ozone measurement. (235.7 GHz, 237.1 GHz, 242.3 GHz, 243.5 GHz, 625.4 GHz, 2.51 THz, 2.54 THz)

HO₂ lines at 649.7 and 660.5 GHz to improve accuracy of HO₂ measurement.

BrO lines at 624.8 and 650.2 GHz to improve accuracy of bromine measurement.

The NRA also lists several other features whose linewidth parameters including temperature dependence are of high priority. These are as follows:

HCN line at 177.3 GHz

CO line at 230.5 GHz

HOCl line at 635.9 GHz

CH₃CN lines at 183.9, 202.3, 624.8, 626.4, and 660.7 GHz

O₃ lines at 239.1, 231.3, 248.2, 249.8, and 250.0 GHz to improve CO retrievals

While these required measurements are for only those transitions which are to be observed from space or which may interfere with observations, additional measurements of these and other transitions for the same molecules would be extremely helpful in extending the very sparse database of linewidths of rotational transitions. In addition, The MLS team needs improved measurements of the non-resonant absorption of water vapor and air throughout these spectral regions. There are measurement programs in progress at our institution and elsewhere which address these requirements, but there remains much to be done in the area of linewidth measurements.

In conjunction with work being done in the kinetics group, we are attempting to obtain definitive identification of the volatile compounds evolved from the solid condensate of the ClO self reaction. This material is trapped at 77K and slowly warmed. Our previous work on the chlorine oxides and oxo-acids provides precise predictions of the rotational spectra of ClOOCl, OClO, ClO, ClClO₂, ClOClO₂, HOCl and HOClO₃. It not only will allow identification of the species, but also will give a moderately good indication of their relative abundances. In our earlier experiments in this laboratory we found only ClOOCl, but those experiments did not involve condensation of products. In our earlier work on OBrO we observed BrO and Br₂O as well as OBrO over a condensate from the reaction of oxygen atoms with Br₂.

An example of another area in which rotational spectroscopy can make a contribution to atmospheric measurements is in the comparison of absorption cross sections in other spectral regions those of rotational transitions. A recent example has recently been reported by Vander Auwera, *et al*⁸³. We are planning simultaneous measurements of the rotational and UV spectra of OBrO in order to obtain an independent measurement of the UV cross section. We have already measured the OBrO permanent dipole moment and can calculate rotational line strength with good accuracy. The amount of OBrO in the optical path can then be determined. Renard, *et al.*^{84,85} have reported detection of stratospheric OBrO in amounts much larger than model calculations would allow⁸⁶. An independent measurement of OBrO cross sections will provide a basis for interpreting atmospheric spectra.

A similar set of measurements would also be useful for OIO. In a paper by Ingham, *et al.*⁸⁷ on the photodissociation of IO and OIO, the uncertainty of

OIO absorption cross section of more than a factor of two is a limiting factor in the precision of the results. Unlike OBrO, our present method of OIO production does not lend itself to dipole moment measurement. We are investigating cleaner and more efficient methods of OIO production. If successful, we shall measure the dipole moment, determine the rotational line strengths, and attempt simultaneous measurements of rotational and UV spectra.

Conclusion

Examples have been presented of studies of rotational spectra which have application to upper atmospheric research. This have been not only applications for interpretation of atmospheric spectra, but also structural studies of molecules which have a role in atmospheric chemistry. It is hoped that the examples and the associated references will be helpful to those wishing to participate in this field of study.

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